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(54) RESIST COMPOSITION AND PATTERN FORMING METHOD USING SAME**(57)Abstract:**

PROBLEM TO BE SOLVED: To suppress the increase of the number of fine particles immediately after production and even after storage over a long period of time by incorporating 2-heptanone as a solvent into a chemical amplification type resist compsn.

SOLUTION: In a resist compsn. contg. at least a medium having such reactivity that solubility to an aq. alkali soln. is varied by reaction with an acid as a catalyst and a water-soluble acid precursor, 2-heptanone is used as a solvent. The amt. of the solvent used is not limited if the solvent is enough to uniformly dissolve the resist compsn. and the solvent is used by such an amt. as to give a desired thickness of a coating film. It is generally used so that the solid content is regulated to 3-50wt.%, preferably 10-30wt.%. When the resultant resist compsn. is used, a part of a semiconductor substrate coated with a resist pattern is made almost free from a gelatinous deposit and pinholes and yield at the time of producing an integrated circuit can be enhanced.

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CLAIMS

[Claim(s)]

[Claim 1] The resist constituent characterized by the above-mentioned solvent being 2-heptanone in the chemistry multiplier system resist constituent containing a medium, a water-soluble acid precursor, and a solvent with the reactivity to which the solubility over an alkali water solution is changed by the reaction which makes an acid a catalyst.

[Claim 2] The resist constituent whose above-mentioned constituent is a positive type chemistry multiplier system resist constituent in claim 1:

[Claim 3] The solubility to 100g of water [in / on claim 1 and / 20 degrees C of the water-soluble above-mentioned acid precursor] is 2.0g. Resist constituent which it is above.

[Claim 4] The resist constituent which is the sulfonium salt by which the water-soluble above-mentioned acid precursor is expressed with a chemical formula (1) in claim 3.

[Formula 1]



(R1 is an alkyl group, a cycloalkyl radical, an aryl group, an alkyl aryl radical, and the permuted alkyl group among a formula, and both R2 and R3 are alkyl groups.) The carbon number of the carbon frame of an alkyl group shows 1-12, and is A~. A trifluoro methansulfonic acid anion, a trifluoro ethane-sulfonic-acid anion, a benzenesulfonic acid anion, a nonafluorobutane sulfonic-acid anion, a toluenesulfonic acid anion, a tetrafluoroboric acid anion, a hexafluoro antimononic acid anion, a hexa fluoroarsenic acid anion, and a hexa fluorophosphoric acid anion are expressed.

[Claim 5] It sets to claims 1 or 2, and the water-soluble above-mentioned acid precursor is 0.4-4 to the whole-quantity 100 weight section of the solvent of a constituent. Resist constituent which carried out weight section combination.

[Claim 6] The pattern formation approach of having the process which forms a pattern by development which uses as a developer the process which uses activity chemical rays for the paint film of the above-mentioned constituent according to claim 1 or 2, and forms a desired pattern latent image, the process which promotes the reaction which makes an acid a catalyst, and an alkali water solution.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the pattern formation approach of having used a resist constituent and it.

[0002]

[Description of the Prior Art] The constituent given [as a chemistry multiplier system resist constituent using an acid catalyzed reaction] in U.S. Pat. No. 3779778, JP,2-27660,B, and JP,2-25850,A is known. These constituents contain the acid precursor which generates an acid in the exposure of radiations, such as a reactant high medium and ultraviolet rays, and an electron ray, under the acid catalyst. This kind of resist makes the pattern latent-image formation section able to generate an acid by the exposure of these radiations, can change the solubility over the developer of the exposure section and the non-irradiated section by the reaction which makes this acid a catalyst, and can obtain a pattern according to a development process.

[0003] These resist constituents are used as a solution which dissolved the acid precursor and the reactant high medium in the suitable solvent. As an acid precursor, the ester of the compound and alkyl sulfonic acid containing two or more onium salt, such as a sulfonate of N-hydroxy imide, various halogenated compounds, a diaryl iodonium salt, and a triarylsulfonium salt, and phenolic hydroxyl groups etc. is usually used. Generally, if there are many poorly soluble things and the solute solvent power of a solvent is low, an acid precursor content will be restricted, or the acid precursor which once dissolved recrystallizes and deposits, and these compounds have the trouble of spoiling the homogeneity of a solution.

[0004] For this reason, as a resist spreading solvent, solvent power, such as the monomethyl of ethylene glycol and the monoethyl ether, ethylene glycol ethyl ether acetate, ethylene glycol methyl ether acetate, a cyclohexanone, and ethyl lactate, was strong, and used the specific thing which has the comparatively high boiling point.

[0005] Furthermore, in a chemistry multiplier system resist, since a reactant high medium and a reactant high acid generator are included under an acid catalyst, when the solvent which has a hydroxyl group is used for the chemical structure, there is an inclination for the hydrogen ion and this constituent which are produced from the solvent to react, and for generation of a particle and change of sensibility to take place. Therefore, it is difficult to use solvents, such as ethylene glycol monomethyl and ethyl ether, and ethyl

lactate.

[0006] On the other hand, the solvent of ketones, such as a cyclohexanone, has high solvent power as compared with ethylene glycol, and the problem called deposit of the acid generator under preservation cannot arise easily. However, own stability of a solvent is bad and there are troubles, such as giving the deposit of a particle and an adhesive fall with a wafer and a resist pattern. Therefore, ethylene glycol methyl ether acetate and ethylene glycol ethyl ether acetate have been widely used as a spreading solvent from the field of preservation stability and solvent power.

[0007] In recent years, it was pointed out that ethylene glycol ether has chronic toxicity, such as a deformed-child delivery and a failure of male infertility, as a bad influence to the body. Taking advantage of this, the change to a safer alternative solvent is demanded of silicon society. The resist constituent using propylene glycol monomethyl ether and propylene-glycol-monomethyl-ether acetate as a solvent with high safety is indicated by JP,3-1659,B and JP,3-6494,B.

[0008] However, since these solvents will increase remarkably while the particulate number in a solution saves if they are used as a solvent of the constituent which consists of a water-soluble acid precursor and a reactant high medium, they form a pinhole and a sludge in the semi-conductor substrate section covered with the resist pattern, and have the problem that a semiconductor integrated circuit reduces the yield at the time of manufacture. Specifically, it is 0.1 micrometers about the propylene-glycol-monomethyl-ether acetate solution containing a resist constituent. After filtering with a membrane filter, the particulate number immediately after manufacture was measured using the Rion automatic particle measuring instrument (KL-20 mold). Consequently, a resist constituent is 0.3 micrometers. The yield was good, when there were few particulate numbers which have the above particle diameter in ten pieces/[ml and] and they manufactured the integrated circuit using this constituent. However, when this constituent was measured after preservation on the 45th and the particulate number was measured in the 24-degree C clean room, it increased from 100 or less particulate numbers/ml for obtaining those with 1200 piece/ml, and the good yield far, and many pinholes and sludges were checked by the semi-conductor substrate section. Thus, propylene glycol alkyl ether was not able to obtain a resist constituent with good preservation stability.

[0009]

[Problem(s) to be Solved by the Invention] The 1st purpose of this invention is offering the spreading constituent of a chemistry multiplier system resist with high preservation stability with few increments in a particulate number, and using this resist constituent, and immediately after the manufacture which solved the technical problem of the conventional technique, and after a mothball are to raise the yield of integrated-circuit manufacture. The 2nd purpose of this invention is to offer the pattern formation approach of making a pattern appearing with high sensitivity and high resolution using the above-mentioned resist constituent.

[0010]

[Means for Solving the Problem] When 2-heptanone was used as a solvent to the resist constituent characterized by including at least a medium with the reactivity to which the solubility over an alkali water solution is changed by the reaction which makes an acid a catalyst, and a water-soluble acid precursor, this invention persons find out giving a good result to solubility and preservation stability, and came to complete this invention.

[0011] If the amount of the above-mentioned solvent used is an amount which is sufficient for dissolving a resist constituent in homogeneity, the amount used is not restricted and can be used in the range in which the spreading thickness of desired thickness is obtained. usually, the range where a formed element becomes 3 ~ 50 % of the weight -- it is preferably used at 10 ~ 30 % of the weight.

[0012] There are what the solubility over an alkali water solution increases as a reactant high medium by the reaction which makes an acid a catalyst, and a thing which decreases. For example, the compound or polymer from which what the solubility over an alkali water solution increases protected the hydroxyl group of alkali fusibility phenol resin, such as a polyvinyl phenol, by the protective groups (an acetal radical, t-butoxycarbonyl group, etc.) which carry out deprotection (separation) according to an acid catalyst is mentioned.

[0013] Moreover, in order to control the alkali solubility of the above-mentioned reactant high medium, alkali fusibility resin can be used if needed. As for alkali fusibility resin, alkali fusibility phenol resin, such as for example, cresol novolak resin, polyvinyl alcohol, polyvinyl alkylether, acrylic resin, a styrene-acrylic-acid copolymer, a styrene maleic anhydride copolymer, a styrene-hydroxystyrene copolymer, polyhydroxy styrene, etc. are mentioned.

[0014] For the water-soluble acid precursor in this invention, the solubility to 100g of water in 20 degrees C is 2.0g. It is desirable to use the above thing. The example of a water-soluble acid precursor has desirable onium salt shown with the following chemical formula (1).

[0015]

[Formula 2]



[0016] With the above-mentioned chemical formula (1), it is R1. It is an alkyl group, a cycloalkyl radical, an aryl group, an alkyl aryl radical, the permuted aryl group, and the permuted alkyl group, and is R2 and R3. They are both alkyl groups. general -- an alkyl group -- 1-12 carbon atoms -- and as for the example, methyl, ethyl, propyl, isopropyl, and butyl are preferably mentioned including 1-4 carbon atoms. As for the substituent of the permuted aryl group, an alkyl group, a halogen atom, an alkoxy group, the amino group, or hydroxyl is mentioned. As for the substituent of the permuted alkyl group, a halogen atom, hydroxyl, the amino group, and an alkoxy group are mentioned.

[0017] A~ in the above-mentioned formula As for an example, a trifluoro methansulfonic acid anion, a trifluoro ethane-sulfonic-acid anion, a benzenesulfonic acid anion, a nonafluorobutane sulfonic-acid anion, a toluenesulfonic acid anion, a tetrafluoroboric acid anion, a hexafluoro antimononic acid anion, a hexa fluoroarsenic acid anion, a hexa fluorophosphoric acid anion, etc. are mentioned.

[0018] As for a water-soluble acid precursor, it is desirable to dissolve and use for a resist constituent to the whole-quantity 100 weight section of 2-heptanone solvent, so that it may become 0.4 ~ 4 weight section. The resist constituent prepared by the concentration of this range is 0.3 micrometers. The particulate number which has the above particle diameter can obtain a resist constituent with good 100 or less preservation [/ml] stability after preservation for 45 days. The inclination which the concentration of a

water-soluble acid precursor increases from 100 or less particulate numbers/ml for obtaining the good yield if [than this range] more far arises, and it is not desirable. Moreover, if fewer than this range, the inclination for sensibility to fall remarkably will arise and the effectiveness of this invention will not be acquired.

[0019] With a resist constituent, the water-soluble above-mentioned acid precursor may be independently used as an acid precursor, and onium salt, such as a sulfonate of N-hydroxy imide, various halogenated compounds, a diaryl iodonium salt, and a triarylsulfonium salt, and a phenolic hydroxyl group may be used combining at least one or more kinds and water-soluble acid precursors, such as ester of the compound and alkyl sulfonic acid which are included.

[0020] The resist constituent of this invention can be made to contain additives, such as the phenolic compound for raising the resist engine performance, a surfactant, a preservation stabilizer, a sensitizer, a striae SHON inhibitor, a plasticizer, and an antihalation agent, if needed.

[0021]

[Embodiment of the Invention] Next, although an example is given and this invention is explained more concretely, this invention is not limited at all by these examples.

[0022] (Example 1) As m, the p-cresol novolak resin:23 weight section, and an acid reactivity medium Pori with a TETORAHIDO pyranil radical (p-vinyl phenol) (90% of rates of installation of a tetrahydropyranil group) : as 2 weight sections and a water-soluble acid precursor Trimethyl sulfonium trifluoromethane sulfonate: 1.2 The Fluorad FC-171(Sumitomo 3M make):0.1 weight section was dissolved as the weight section, the 2-heptanone:75 weight section, and an anti-striae SHON agent, and the positive-resist constituent was prepared.

[0023] 0.1 After filtering with the membrane filter of mum, the particulate number of the solution immediately after manufacture was measured using the Rion automatic particle measuring instrument (KL-20 mold). Consequently, 0.3 The particle number more than mum was 12 pieces/ml. As a result of measuring this constituent after preservation for 45 days and measuring a particulate number in a 24-degree C clean room, the particulate number was 25 pieces/ml.

[0024] Next, 120 degrees C of above-mentioned resist liquid were heat-treated for this constituent for 2 minutes after dropping and rotation spreading on the silicon wafer, and the resist film with a thickness of 1 micrometer was obtained. Electron-beam-lithography equipment (the acceleration voltage of an electron ray is 50kV) was used for this substrate, the dose was changed gradually, was heat-treated for 2 minutes 100 degrees C after electron beam irradiation, and the acid catalyzed reaction of the latent-image part of a resist was promoted.

[0025] After above-mentioned heat treatment and tetramethylammonium hydroxide 2.38 The resist which used the water solution containing weight % for the developer, and formed the latent image was developed for 120 seconds. And when asked for a remaining rate of membrane and sensibility, a remaining rate of membrane is 98%, and it was checked that sensibility (the minimum dose from which the thickness of a resist is set to 0) becomes 3.0microC/cm2 of high sensitivity from the sensibility (4.0microC/cm2) of the resist constituent which uses ethylene glycol methyl ether acetate as a solvent.

[0026] Moreover, electron-beam-lithography equipment was used for the semi-conductor substrate which applied the resist solution of this invention, the 0.5-micrometer pattern was drawn on the resist film, and the 0.5-micrometer resist pattern was obtained. In this substrate, as a result of an optical microscope's

investigating the existence of a pinhole and a gel sludge, the pinhole and the sludge were not checked, but the yield at the time of integrated-circuit production was good.

[0027] (Example 2) In the example 1, it replaced with trimethyl sulfonium trifluoromethane sulfonate as a water-soluble acid precursor, and carried out according to the approach of an example 1 except having used dimethylphenyl sulfonium trifluoromethane sulfonate. The particulate number of the solution immediately after manufacture was ten pieces/ml. As a result of measuring this constituent after preservation for 45 days and measuring a particulate number in a 24-degree C clean room, the particulate number was 20 pieces/ml.

[0028] Moreover, like the example 1, when a remaining rate of membrane and sensibility were measured, a remaining rate of membrane is 98%, and it was checked that sensibility turns into high sensitivity compared with the sensibility of the resist constituent which uses 1.4micro of C/cm² and ethylene glycol methyl ether acetate as a solvent. Furthermore, when the pinhole and the gel sludge were checked like the example 1, they were not observed but were very stable solutions.

[0029] (Example 3) In the example 1, it carried out according to the approach of an example 1 except having used water-soluble acid precursor trimethyl sulfonium p-toluene sulfonate instead of acid precursor trimethyl sulfonium trifluoromethane sulfonate. Consequently, the above-mentioned resist filtered, and the particulate number of 45 days after is 36 pieces/ml, and it showed the sensibility of 3.5microC/cm².

[0030] (Example 4) At an example 1, it is the 1 and 8-North America Free Trade Agreement RUIMIJIRU trifluoromethane sulfonate:0.6 weight section and trimethyl sulfonium trifluoromethane sulfonate:0.6 instead of acid precursor trimethyl sulfonium trifluoromethane sulfonate. Except having used the acid precursor which mixed the weight section, it carried out according to the approach of an example 1. Consequently, the above-mentioned resist filtered, and the particulate number of 45 days after is 22 pieces/ml, and it showed the high sensitivity of 1.5microC/cm².

[0031] (Example 5) At an example 1, it is triester:0.6 of pyrogallol and ethane sulfonic acid instead of acid precursor trimethyl sulfonium trifluoromethane sulfonate. The weight section and trimethyl sulfonium trifluoromethane sulfonate: 0.6 Except having used the acid precursor which mixed the weight section, it carried out according to the approach of an example 1. Consequently, it filters, the particulate number of 45 days after is 22 pieces/ml, and the above-mentioned resist is 2.0microC/cm². High sensitivity was shown.

[0032] (Example 6) : which has a t-butoxycarbonyl group as an acid reactivity medium (90% of rates of installation of a t-butoxycarbonyl group) (p-vinyl phenol) — as 3 weight sections, m, the p-cresol novolak resin:27 weight section, and an acid precursor — the trimethyl sulfonium trifluoromethane sulfonate:1.0 weight section, the 2-heptanone:70 weight section, and an anti-striae SHON agent — FC-171:0.1 The solution which consists of the weight section was prepared.

[0033] The particulate number of the solution immediately after manufacture was 25 pieces/ml. As a result of measuring this constituent after preservation for 45 days and measuring a particulate number in a 24-degree C clean room, the particulate number was 50 pieces/ml.

[0034] When this resist was asked for sensibility and a remaining rate of membrane like the example 1, sensibility (the minimum exposure from which the thickness of a resist is set to 0) is C/cm² 10micro. The remaining rate of membrane was 95%. After using electron-beam-lithography equipment on the semi-conductor substrate which applied the above-mentioned resist solution and drawing 15micro of

0.5-micrometer patterns with the exposure of C/cm^2 , when the pinhole and the gel sludge were checked like the example 1, they were not observed but were very stable solutions.

[0035]

[Effect of the Invention] The resist constituent of this invention has very few particulate numbers immediately after manufacture, and also after the mothball, there are few increments in a particle and they are excellent at preservation stability. Moreover, if the resist constituent of this invention is used, since there will almost be no generating of a gel sludge and a pinhole in the semi-conductor substrate part covered by the resist pattern, the yield at the time of integrated-circuit manufacture can be made good, and it is industrially advantageous.

[Translation done.]